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Fundamental Studies on Electrolytic Manufacturing of Chlorate with Magnetite Anode.

(11). Mechanism of Perchlorate Formation

(Received Apr. 20 1950)

Takashi Nagai*

Abstract

The effect of perchlorate by-product in electrolytic manufacturing of chlorate with Japanese magnetite anode was reported on my last paper⁽¹⁾. This investigation was performed to obtain the relationship between the anode potential and the amount of produced perchlorate in the electrolysis of chlorate solution, especially in case when catalysts for the decomposition of hydrogen peroxide were added.

From the experimental results it is postulated that chlorate may be oxidized to perchlorate by the hydrogen peroxide produced at the anode

Introduction

When the electrolytic oxidation is thermodynamically irreversible, as is the case in the oxidation of chlorate to perchlorate, the phenomena are very complex and no satisfactory theory for the electrochemical reaction has ever been presented.

Generally, it has been believed that a high anode potential may oxidize more intensively than a low one. Glasstone and Hickling⁽²⁾ showed that this theory is not applicable for many irreversible electrolytic oxidations and presented the theory of anode formation of hydrogen peroxide. The author of this paper has studied the electrolytic oxidation reaction forming chlorate into perchlorate with magnetite or platinum anode and as a result concluded that the hydrogen peroxide theory is valid for this reaction.

Experimental

(1) The resistance of the magnetite anode; It was necessary for us to know the resistance of the magnetite in order to obtain the anode potential at the electrode surface during electrolysis.

Then the potential difference between two points on the electrode were measured potentiometrically when various currents passed. The data are recorded in Table 1.

From these data the mean specific resistance of magnetite electrode was found to be 0.282 ohm cm. Since it is small,

Table 1 The Resistance of Magnetite

Current (A)	Potential Drop (V)	Resistance (
0.01	0.0027	0.270
0.02	0.0050	0.250
0.03	0.0073	0.243
0.04	0.0094	0.235
0.05	0.0118	0.236
0.06	0.0140	0.233
0.08	0.0218	0.272
0.10	0.0236	0.236
0.20	0.0496	0.248
0.30	0.0714	0.238
0.40	0.0994	0.248
0.50	0.1177	0.235
0.60	0.1407	0.234
0.80	0.1840	0.230
1.00	0.2230	0.223

mean value 0.
specific resistance 0.282

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(1) C. Fujioka and T. Nagai: *Proe. Faculty of Eng. Keio Univ.* (19)

(2) Glasstone: *Chem. Rev.*, 25 (1939) 407.

it may be possible to neglect the potential drop in the anode in electrolysis.

(2) Measurement of the potential of magnetite and platinum anode; A magnetite or a platinum plate, which was shielded by paraffin with one square centimeter window, was placed in a cell containing 50-ml of 60% sodium chlorate solution. Iron plate was used as the cathode. The potential was measured using normal calomel electrode as auxiliary cell.

(3) Current efficiency; After electrolysis the produced perchlorate was analysed and the mean current efficiency of the oxidation chlorate was obtained. The method of analysis was the same as that reported on my last paper.

Results and Discussion

(1) Time influence on anode potential at constant current density; Potentials of both magnetite and platinum anodes were measured at constant time intervals. The results are shown on Table 2 and Fig 1.

Table 2. Time Influence on Anode Potential at Constant Current Density

Current Density (A/dm ²)		Anode Potential E _N -calomel (volt) at 17°C in 65% NaClO ₃ solution									
		0.14		0.2		0.3		1.0		10.	
		Magnetite		Platinum		Magne- tite	Magne- tite	Platinu- m	Magne- tite	Platinu- m	Magne- tite
Acidity	Acidic	Basic	Acidic	Basic	Acidic	Acidic	Acidic	Acidic	Acidic	Acidic	
Time (minutes)	1				1.470	0.44	1.54		1.642		
	2	0.070	-0.242	1.484	1.520	0.58	1.56	1.784	1.640	1.944	2.012
	3	0.090	-0.231	1.512	1.544	0.65	1.57	1.808	1.640	1.954	
	4	0.110	-0.221	1.526	1.556	0.68	1.57	1.818	1.638	1.959	2.012
	5	0.143	-0.204	1.542	1.568	0.70	1.57		1.636	1.963	2.010
	6	0.168	-0.172	1.554	1.574	0.73	1.57	1.828	1.637	1.966	2.006
	7	0.184	-0.130	1.564	1.578	0.729	1.57		1.636	1.968	2.004
	8	0.194	-0.084	1.570	1.581	0.711	1.568	1.840	1.636	1.968	2.004
	9	0.210	-0.053	1.578	1.586	0.687	1.560		1.637	1.968	1.995
	10	0.217	-0.010	1.582	1.588	0.690	1.552	1.848	1.635	1.968	1.990
	12	0.225	0.090	1.588	1.590	0.694	1.548	1.856		1.968	1.990
	14	0.229	0.134	1.594	1.594	0.694	1.548	1.861		1.969	1.988
	16	0.229	0.126	1.596	1.595	0.766	1.552	1.867			
	18	0.221	0.068	1.599	1.598	0.648	1.550	1.872			
	20	0.225	0.063	1.599	1.598	0.625	1.550	1.876			
22	0.211	0.062			0.593		1.882				
24	0.207	0.062			0.568						
26	0.197	0.057			0.520		1.883				
28	0.183	0.050			0.490		1.885				
30		0.040			0.460						

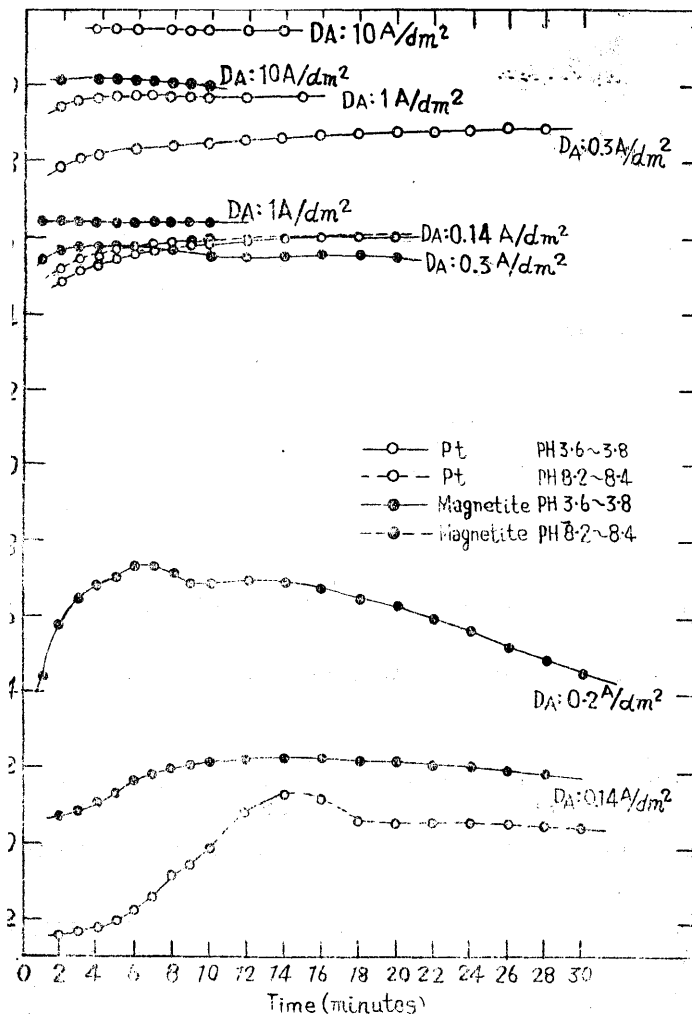


Fig. 1. Time Influence on Anode Potential
chlorate solution (pH 5.2-5.4). In these measurements electrolyte with the constant composition was prepared in order to exclude the effect of the composition variation. The results are given in Table 3 and Fig 2.

Using platinum as the anode, logarithms of current and anode potential have linear relationship, but on the other hand, using magnetite, the curve deviated from a straight line. Moreover, at low current densities potentials of magnetite anode are lower than those of platinum, but at very high current densities the former are higher than the latter. In spite of the above facts the oxidation ability of magnetite is generally far weaker than that of platinum. Then it may be postulated that it is incorrect to decide the oxidation reaction by anode potential only.

(3) Influence of catalysts for decomposing the hydrogen peroxide on the electrolytic oxidation of sodium chlorate; To find the mechanism of the electrolytic oxidation of chlorate, the relation between the anode potential and the oxidation efficiency was investigated when the catalysts for the decomposition of hydrogen peroxide were added. As the catalysts 0.001 mol. copper sulfate and manganese

Using platinum as the anode, the potential becomes higher with the elapse of time, but the increasing rate becomes gradually small. That is, it has a saturation curve.

On the other hand, using magnetite, the potential reaches a maximum and then decreases with time.

The curve for magnetite anode, however, approaches a saturation when the anode current density is high. No effect of acidity on the anode potential was found, but at low current density some potential difference was appreciable in case of magnetite.

(2) Anode potentials at various current densities; Taking account of the results obtained above, the potentials reached their maximum values were measured at various current densities in electrolysis of

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Table 3 Anode Potentials at Various Current Densities

in 60% NaClO ₃ Solution (PH. 5.2~5.4)					
Current Density		Magnetite Anode		Platinum Anode	
I (A/dm ²)	log I	Potential E _N -calomel (volt)	Temperature(°C)	Potential E _N -calomel (volt)	Temperature(°C)
0.2	-0.699			1.852	16
0.4	-0.398			1.902	16
1	0.000	1.528	16	1.956	16
2	0.301	1.568	16	2.001	16
4	0.602	1.640	16	2.058	16
10	1.000	1.800	17	2.136	16
20	1.301	1.960	17		
30	1.477	2.140	17	2.208	17
40	1.602	2.220	18		
61	1.785	2.580	19	2.274	19
76	1.881	2.620	20		
100	2.000			2.284	20

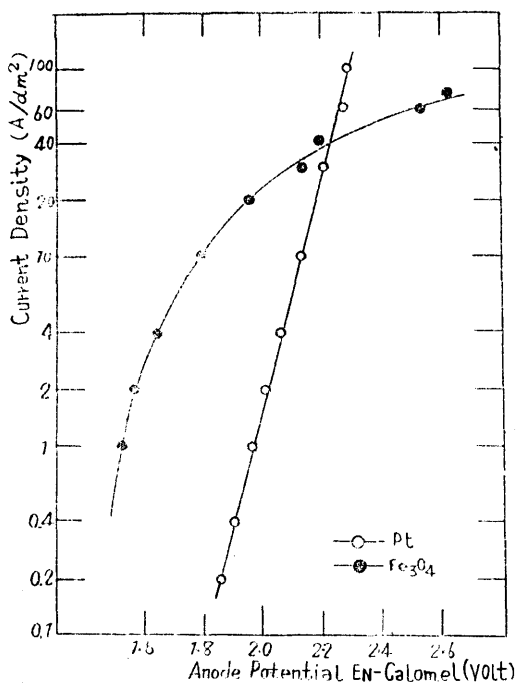


Fig. 2 Anode Potential at Various Current Densities sulfate were added to 100 ml. solution. The oxidation efficiency was determined by its mean value for the oxidation of chlrate. The results are shown in Table 4 and Fig 3.

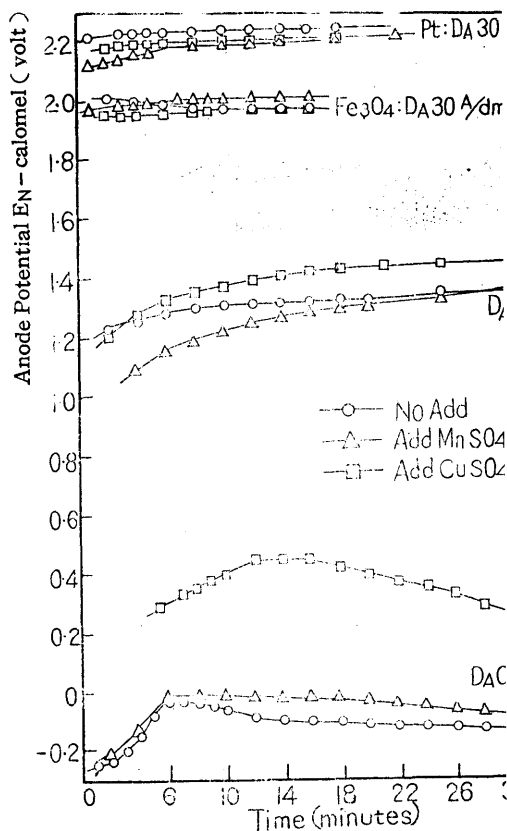


Fig. 3. Influence of Catalysts for Decomposing the I Peroxide on the Electrolytic Oxidation of Sodium C (13).

Table 4. Influence of Catalysts for Decomposing the Hydrogen Peroxide on the Electrolytic Oxidation of Sodium Chlorate

Current density (dm ²)	Magnetite Anode Potential E _N -calomel (volt)						Platinum Anode Potential E _N -calomel (volt)					
	0.14 (at 20°C)			30 (at 16~17°C)			0.14 (at 20°C)			30 (at 16~17°C)		
Current density (0.1M/l)	no	Mn ⁺⁺	Cu ⁺⁺	no	Mn ⁺⁺	Cu ⁺⁺	no	Mn ⁺⁺	Cu ⁺⁺	no	Mn ⁺⁺	Cu ⁺⁺
1	-0.240				1.966					2.222	2.128	
2	-0.220	-0.210		2.004	1.980	1.954	1.225		1.200		2.126	2.180
3	-0.190				1.980	1.953				2.228	2.140	2.190
4	-0.140	-0.130		1.992	1.992	1.956	1.265	1.090	1.275	2.232	2.160	2.192
5	-0.070		0.290		1.992					2.232	2.164	2.196
6	-0.024	-0.020	0.300	1.986	1.992	1.960	1.286	1.150	1.325	2.236		2.196
7	-0.024		0.328		1.998							
8	-0.033	-0.015	0.357	1.972	2.004	1.964	1.290	1.185	1.352	2.236	2.172	2.196
9	-0.044		0.380		2.004	1.966						
10	-0.053	-0.008	0.390	1.976	2.003	1.965	1.303	1.220	1.376	2.240		2.194
12	-0.080	-0.020	0.453	1.978	2.000	1.965	1.306	1.245	1.393	2.236	2.180	2.200
14	-0.093	-0.020	0.451	1.976	2.002	1.964		1.264	1.408	2.240		2.198
16	-0.097	-0.051	0.460	1.976	2.000	1.963	1.315	1.280	1.420	2.240		
18	-0.100	-0.021	0.422				1.320	1.295	1.429	2.240	2.222	2.220
20	-0.104	-0.032	0.407				1.313	1.309	1.434			
22	-0.108	-0.045	0.381								2.222	
24	-0.110	-0.060	0.360									
26	-0.114	-0.069	0.334									
28	-0.118	-0.074	0.286									
30	-0.122	-0.082	0.271				1.351	1.360	1.457			
60							1.415	1.423	1.460			
180												
Mean Current Efficiency for NaClO ₃ →NaClO ₄ (%)				3.6	1.9	3.5				54	29	42

* 60% NaClO₃ Solutions (pH 5.2~5.4) were used

At low current densities and when the catalysts were added, the anode potentials were higher than when they were not. This was the same for both anodes. Even at high current densities the potential difference between these two anodes was not appreciable. Therefore it may be supposed that there is no influence of catalysts on anode potential. Oxidation efficiencies, however, decreased when catalysts were added, especially in case manganous sulfate was added. From the facts mentioned above, the following mechanism of oxidation of chlorate is presumed: first, hydroxyl ions discharge at anode to produce hydroxyl radicals, which immediately combine themselves to form hydrogen peroxide, and hydrogen peroxide thus produced may oxidize chlorate changing it into perchlorate. If the catalysts of decom-

osition for hydrogen peroxide are present, the hydrogen peroxide will decompose to give oxygen and water, and the oxidation efficiency decreases. Anode potential may have no direct relation to the oxidation reaction.

Summary

We investigated the mechanism of perchlorate formation in electrolysis of chlorate with magnetite and platinum anode. Anode potentials were measured at various current densities in electrolysis of chlorate and it was found that at high current densities the potential of magnetite was higher than that of platinum. And it is postulated that the anode potential has no direct effect on the oxidation reaction. The influence of catalysts for decomposing the hydrogen peroxide on oxidation efficiency and anode potential were investigated, and from the results it was found that the hydrogen peroxide theory presented by Glasstone and coworkers was valid for this oxidation reaction.

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